

UV RESISTANT RESIN FOR PARAFFINIC SOLVENT BASED PAINT

Background of the Invention

Standard mineral spirits used in making typical interior and exterior paint
5 formulations normally contain about 20 percent aromatic compounds. For various
reasons, including environmental and ecological concerns, there is a current demand for
paint resins that are soluble in paraffinic solvents which do not contain aromatic
compounds. However, it is also important for the resin used in such applications to
maintain a high level of hardness and ultra-violet light resistance. This desirable
10 combination of properties has heretofore been elusive. More specifically, in the past it has
only been possible to improve solubility in paraffinic solvents by compromising hardness
and/or ultra-violet light (UV) resistance.

United States Patent 5,496,905 and United States Patent 5,504,143 disclose a
resin for paints which is highly soluble in paraffinic solvents and which has good resistant
15 to ultra-violet light. These resins contain from about 10 weight percent to about 55
weight percent para-tertiary-butyl styrene (PTBS). These resins also contain about 20
weight percent to about 80 weight percent of at least one alkyl methacrylate monomer,
from about 2 weight percent to about 25 weight percent alkyl acrylate monomer, and
optionally up to about 40 weight percent of a vinyl aromatic monomer in addition to the
20 PTBS. However, despite the fact that the resin described in United States Patent
5,496,905 and United States Patent 5,504,143 has good resistance to ultra-violet light
coatings made therewith tend to yellow and discolor over time with exposure to ultra-
violet light

Summary of the Invention

This invention disclose a resin for paints which is highly soluble in paraffinic
solvents and which has excellent resistance to ultra-violet light. Coatings made with these
resins are highly resistant to yellowing and discoloration on exposure to ultra-violet light
over long periods of time. These resins are comprised of repeat units which are derived
30 from (a) about 5 to about 60 weight percent tertiary-butyl cyclohexyl methacrylate, (b) 0
to about 40 weight percent vinyl aromatic monomers, (c) about 20 to about 80 weight
percent alkyl methacrylate monomers, and (d) about 1 to about 30 weight percent alkyl

acrylate monomers.

This invention more specifically discloses a resin which is particularly useful in making paraffinic solvent based paints, said resin being comprised of repeat units which are derived from (a) about 5 to about 60 weight percent tertiary-butyl cyclohexyl methacrylate, (b) 0 to about 40 weight percent vinyl aromatic monomers, (c) about 20 to about 80 weight percent alkyl methacrylate monomers, and (d) about 1 to about 30 weight percent alkyl acrylate monomers.

The subject invention further discloses a paint formulation which is comprised of (a) a paraffinic solvent; (b) a resin which is comprised of repeat units which are derived from (i) about 5 to about 60 weight percent tertiary-butyl cyclohexyl methacrylate, (ii) 0 to about 40 weight percent vinyl aromatic monomers, (iii) about 20 to about 80 weight percent alkyl methacrylate monomers, and (iv) about 1 to about 30 weight percent alkyl acrylate monomers; and (c) one or more pigments.

Detailed Description of the Invention

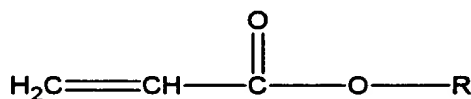
The paint resins of this invention are synthesized utilizing free radical emulsion polymerization techniques. This is carried out by adding a tertiary-butyl cyclohexyl methacrylate (TBCHMA), optionally vinyl aromatic monomers, an alkyl methacrylate monomer, and an alkyl acrylate monomer to water to form an aqueous polymerization medium. The aqueous polymerization medium will also normally contain a required amount of a surfactant. Polymerization of the monomers is then initiated with a free radical generator to produce a latex of the resin. The latex made is subsequently coagulated to recover the resin.

In synthesizing the resins of this invention generally from about 5 weight percent to about 60 weight percent TBCHMA, from about 20 weight percent to about 80 weight percent alkyl methacrylate monomers, from about 2 weight percent to about 30 weight percent alkyl acrylate monomers, and from 0 to about 40 weight percent vinyl aromatic monomers are polymerized. It is generally preferred to limit the quantity of vinyl aromatic monomers in the resin since they normally lead to a reduced level of ultra-violet light resistance. For instance, vinyl aromatic monomers can be totally eliminated from the resin. In any case, these resins can be used in manufacturing paints for interior and exterior coatings.

In making resins for interior coatings normally from about 5 weight percent to about 40 weight percent TBCHMA, from about 25 weight percent to about 80 weight percent alkyl methacrylate monomers, from about 5 weight percent to about 25 weight percent alkyl acrylate monomers, and from 0 to about 40 weight percent vinyl aromatic monomers are polymerized. Resins for interior paints preferably contain from about 15 weight percent to about 35 weight percent TBCHMA, from about 30 weight percent to about 70 weight percent alkyl methacrylate monomers, from about 10 weight percent to about 25 weight percent alkyl acrylate monomers, and from 0 to about 35 weight percent vinyl aromatic monomers.

In making resins for exterior coatings normally from about 10 weight percent to about 60 weight percent TBCHMA, from about 30 weight percent to about 80 weight percent alkyl methacrylate monomers, from about 1 weight percent to about 20 weight percent alkyl acrylate monomers, and from 0 to about 15 weight percent vinyl aromatic monomers are polymerized. Resins for exterior paints preferably contain from about 10 weight percent to about 30 weight percent TBCHMA, from about 50 weight percent to about 80 weight percent alkyl methacrylate monomers, from about 2 weight percent to about 10 weight percent alkyl acrylate monomers, and from 0 to about 10 weight percent vinyl aromatic monomers.

The alkyl acrylate monomers that can be used in the resins of this invention generally have the structural formula:

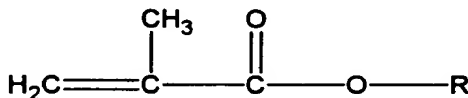


wherein R represents an alkyl group containing from 1 to 10 carbon atoms. The alkyl group in such alkyl acrylate monomers will preferably contain from 2 to 8 carbon atoms with alkyl groups that contain 8 carbon atoms being most preferred. Accordingly, ethyl acrylate, propyl acrylate, butyl acrylate, pentyl acrylate, hexyl acrylate, and 2-ethyl hexyl acrylate are preferred alkyl acrylate monomers with 2-ethylhexyl acrylate being the most preferred. The alkyl groups in such alkyl acrylate monomers can be straight chained or branched. Thus, normal-propyl acrylate, isopropyl acrylate, normal-butyl acrylate, or

tertiary-butyl acrylate can be employed.

The vinyl aromatic monomers which can optionally be included include all of those which are known to polymerize in free radical systems. Such vinyl aromatic monomers typically contain from 8 to 20 carbon atoms. Usually, the vinyl aromatic monomer will contain from 8 to 14 carbon atoms. Some representative examples of vinyl aromatic monomers that can be utilized include styrene, 1-vinyl naphthalene, 2-vinyl naphthalene, 3-methyl styrene, 4-propyl styrene, 4-cyclohexyl styrene, 4-dodecyl styrene, 2-ethyl-4-benzyl styrene, 4-(phenylbutyl) styrene, para-tertiary-butyl styrene, and the like. Styrene, para-methyl styrene, and mixtures of para-methyl styrene and ortho-methyl styrene are generally the most preferred vinyl aromatic monomers.

The alkyl methacrylate monomers that can be used have the structural formula:



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wherein R represents an alkyl group containing from 1 to 10 carbon atoms ($\text{R}=\text{C}_n\text{H}_{2n+1}$ with n being an integer from 1 to 8). The alkyl groups in such alkyl methacrylate monomers can be straight chained or branched. Methyl methacrylate, ethyl methacrylate, propyl methacrylate, isobutyl methacrylate, and n-butyl methacrylate are representative examples of alkyl methacrylate monomers that can be used. The alkyl group in the alkyl methacrylate monomer will preferably contain from 1 to 4 carbon atoms with alkyl groups which contain 4 carbon atoms being most preferred. Accordingly, isobutyl methacrylate is a highly preferred monomer.

Essentially any type of free radical generator can be used to initiate such free radical emulsion polymerizations. For example, free radical generating chemical compounds, ultra-violet light or radiation can be used. In order to ensure a satisfactory polymerization rate, uniformity, and a controllable polymerization, free radical generating chemical agents which are water soluble under the polymerization conditions are generally used with good results.

~~Some representative examples of free radical initiators which are commonly used include the various peroxygen compounds such as potassium persulfate, ammonium~~

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~~persulfate, benzoyl peroxide, hydrogen peroxide, di-t-butyl peroxide, dicumyl peroxide,~~
2,4-dichlorobenzoyl peroxide, decanoyl peroxide, lauryl peroxide, cumene hydroperoxide,
p-menthane hydroperoxide, t-butyl hydroperoxide, acetyl acetone peroxide, dicetyl
peroxydicarbonate, t-butyl peroxyacetate, t-butyl peroxy maleic acid, t-butyl
peroxybenzoate, acetyl cyclohexyl sulfonyl peroxide, and the like; the various azo
compounds such as 2-t-butylazo-2-cyanopropane, dimethyl azodiisobutyrate,
4,4'-azobis(4-cyanovaleric acid), Azo carboxy valeric acid, azodiisobutyronitrile, 2-t-
butylazo-1-cyanocyclohexane, 1-t-amylazo-1-cyanocyclohexane, and the like; the various
alkyl perketals, such as 2,2-bis-(t-butylperoxy)butane, ethyl 3,3-bis(t-
butylperoxy)butyrate, 1,1-di-(t-butylperoxy) cyclohexane, and the like. Persulfate
initiators, such as potassium persulfate and ammonium persulfate are especially useful in
such aqueous emulsion polymerizations.

The amount of initiator employed will vary with the desired molecular weight of
the resin being synthesized. Higher molecular weights are achieved by utilizing smaller
quantities of the initiator and lower molecular weights are attained by employing larger
quantities of the initiator. However, as a general rule from 0.005 to 1 phm (parts by
weight per 100 parts by weight of monomer) of the initiator will be included in the
reaction mixture. In the case of metal persulfate initiators most commonly from 0.1 to 0.5
phm will be employed in the polymerization medium.

The emulsifiers used in the polymerizations of this invention may be charged at the
outset of the polymerization or may be added incrementally or proportionately as the
polymerization reaction proceeds. A wide variety of types of emulsifiers or surfactants,
such as anionic, cationic, nonionic and amphoteric emulsifiers, can be utilized in the
process of this invention. Rosin acid or fatty acid emulsifiers are normally utilized.

Synthetic surfactants can also be used. For instance, salts of alkyl sulfates, alkyl
sulfonates and alkyl phosphates can be employed as the emulsifier. The alkyl groups in
these compounds generally contain from 1 to 30 carbon atoms. Normally the alkyl
groups in these surfactants will contain from 8 to 20 carbon atoms. The surfactant
utilized will normally be a sodium, potassium, magnesium or ammonium salt. Sodium
lauryl sulfate, ammonium lauryl sulfate, sodium dodecyl benzene sulfonate, and sodium
dodecyl sulfate are some representative examples of highly suitable emulsifiers.

Generally from about 1.5 phm to about 8 phm of emulsifier is utilized in preparing

the aqueous polymerization medium. In most cases, it will be preferred to utilize from about 4 phm to 6.5 phm of emulsifier. It is normally more preferred to utilize from about 5.5 phm to about 6.5 phm of the emulsifier. The precise amount of emulsifier required in order to attain optimal results will, of course, vary with the specific emulsifier being used.

5 However, persons skilled in the art will be able to easily ascertain the specific amount of emulsifier required in order to attain optimal results.

The free radical emulsion polymerization will typically be conducted at a temperature that is within the range of about 20°C to about 95°C. It is generally preferred for the polymerization to be carried out at a temperature that is within the range

10 of 30°C to about 80°C. It is typically more preferred to utilize a polymerization temperature that is within the range of about 45°C to about 70°C. To increase conversion levels, it can be advantageous to increase the temperature as the polymerization proceeds. For instance, it is desirable for the polymerization temperature could be maintained at about 45°C at the beginning of the polymerization and increased to

15 a final temperature of about 70°C at the end of the polymerization. After the polymerization has been completed the resin can be recovered from the latex by using standard coagulation and drying techniques.

The resins of this invention can be employed in manufacturing paraffinic solvent based paints. These paints utilize organic solvents that contain virtually no aromatic compounds. For instance, the paraffinic solvents employed in making the paints of this

20 invention will normally contain less than about 2 weight percent aromatic compounds. It is normally preferred for the organic solvent used in making such paints to contain less than about 1 percent aromatic compounds.

The paints of this invention are comprised of the paraffinic solvent, the resin, and

25 one or more pigments. Such paints can optionally contain fillers, plasticizers, stabilizers, dryers, fungicides, insecticides, antifouling agents, and anticorrosive agents.

Pigments are normally added to paint formulations to impart color and hiding power to the coating. Titanium dioxide is an example of a widely used pigment that imparts hiding power and a white color. Mineral pigments, such as oxides of iron and

30 chromium, organic pigments, such as phthalocyanine, and active anticorrosive pigments, such as zinc phosphate, are representative examples of other widely used pigments.

Fillers are normally inexpensive materials that are added to the paint formulation

to attain the desired consistency and non-settling characteristics. Fillers can also improve a coatings physical properties, such as resistance to cracking and abrasion. Some representative examples of widely utilized fillers include chalks, calcium carbonates, clays, micas, forms of barites and talcs, and silica.

5 Driers are chemical compounds, such as salts of cobalt, lead, manganese, barium, and zinc, which speed up drying. Plasticizers are agents which control the hardness of the film or which impart flexibility. Stabilizers are chemical agents that neutralize the destructive effects of heat and ultraviolet light. Fungicides and insecticides are commonly added to interior and exterior house paints. Antifouling compounds are commonly added
10 to marine paints to inhibit marine growth.

This invention is illustrated by the following examples that are merely for the purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it can be practiced. Unless specifically indicated otherwise, all parts and percentages are given by weight.

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Example 1

In this experiment a resin for interior coatings was synthesized by polymerizing TBCHMA, isobutyl methacrylate, and 2-ethylhexyl acrylate. In the procedure used 124.05 phm (parts by weight per 100 parts by weight of monomer) of water, 0.4 phm of
20 potassium hydroxide (45% active), 0.52 phm of anhydrous sodium sulfate, 5 phm of rosin acid soap, 6 phm of 5% active potassium persulfate initiator solution, 30 phm of TBCHMA, 60 phm of isobutyl methacrylate, 10 phm of 2-ethylhexyl acrylate, and 0.5 phm of t-dodecyl mercaptan were charged into a polymerization reactor. The temperature at the start of the polymerization was about 45°C. During the polymerization
25 the temperature of the polymerization medium increased to about 68°C over a period of about 6 to 7 hours. The latex prepared by this procedure was subsequently coagulated with the resin made being recovered.

The solution and polymer properties of the resin made were then determined and compared with those of Plioway® EC1 resin, Plioway® U200 resin, and Pliolite® AC80
30 resin. Plioway® EC1 resin is made by The Goodyear Tire & Rubber Company using the same procedure as was utilized in this experiment except that para-methyl styrene is employed in place of the TBCHMA. Plioway® U200 resin is made by The Goodyear Tire

& Rubber Company using the same procedure as was utilized in this experiment except that para-tertiary butyl styrene (PTBS) and para-methyl styrene are employed in place of the TBCHMA. Pliolite® AC80 resin is made by The Goodyear Tire & Rubber Company using the same procedure as was utilized in this experiment except that styrene is employed in place of the TBCHMA.

The properties of the TBCHMA containing resin made in this experiment, the Plioway® EC1 resin, and the Plioway® U200 resin are shown in Table I. The Pliolite® AC80 resin was insoluble in Exxsol D40 solvent and Isopar G solvent. Accordingly, the Pliolite AC80 resin was not compared with the other resins in Table I.

The Ford cup viscosity at 20°C of the 20 weight percent TBCHMA containing resin, the Plioway® EC1 resin, and the Plioway® U200 resin in both Isopar G solvent and Exxsol D40 solvent are shown in Table I. It should be noted that Exxsol D40 solvent contains less than one percent aromatics and that Isopar G contains virtually no aromatic compounds.

Table I also shows the C.S.T. of 20 weight percent solutions of the three resins in Isopar G solvent and Exxsol D40 solvent. The C.S.T. temperatures reported in Table I were determined by slowly cooling down the polymer solution and recording the point at which cloudiness appears. This point is determined by recording the transmittance of a light beam passing through the solution. When the cloud point is reached, the transmittance sharply decreases. As can be seen from these CST values in Table I the TBCHMA containing resin is much more soluble in these nonaromatic solvents than is the Plioway® EC1 resin.

The weight average molecular weight (Mw), number average molecular weight (Mw), polydispersity (Pd), and glass transition temperature (Tg) of the resins are also reported in Table I.

Table I

Property	TBCHMA Resin	EC1 resin	U200 resin
Viscosity in ISOPAR G	36 sec	20 sec	18 sec
Viscosity in EXXOL D40	33 sec	19 sec	16 sec
C.S.T. in ISOPAR G	-22°C	14°C	-6°C
C.S.T. in EXXOL D40	-30°C	-7°C	-25°C
Mw	242,000	100,000	180,000
Mn	62,000	40,000	50,000
Pd	3.9	2.9	3.6
Tg (midpoint)	51°C	56°C	56°C

It is normally important for the resin to have a glass transition temperature of greater than about 50°C to insure satisfactory hardness. The resin made with the TBCHMA had a glass transition temperature (midpoint) of 51°C which is indicative of good hardness.

Clear films of the TBCHMA containing resin and Plioway U200 resin were prepared by evaporation of solutions in Isopar G. Table II illustrates the resistance to yellowing Delta b* (in the L*, a*, b* system) under ultraviolet light for six weeks of the pure resins. As can be seen from Table II, the TBCHMA containing resin was very resistant to yellowing whereas the Plioway® U200 resin yellowed with continuing exposure to the ultra-violet light.

Table II

UV Exposure Time	TBCHMA Resin	Plioway® U200 resin
none	0	0
1 week	<0.5	2
2 weeks	<0.5	3.5
3 weeks	<0.5	6
4 weeks	<0.5	8
5 weeks	<0.5	9
6 weeks	<0.5	10.5

While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention.